

ULTRAFINE PARTICLES OF IRON IN FISCHER-TROPSCH SYNTHESIS

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INTRODUCTION

Though direct combustion of natural gas is the most efficient use of this abundant, inexpensive, and cleaner fossil fuel, its potential to replace existing less efficient feedstocks for downstream processes is enormous. Direct conversion of methane to useful products under mild conditions is an ongoing area of research, and a few reported successes include higher hydrocarbons (C_2 - C_6) synthesis on Pt at 250°C,¹ Hg-catalyzed synthesis of methanol at 180°C,² and acetic acid synthesis catalyzed by aqueous $RhCl_3$ at 100°C.³ Since these approaches are in early stages of development, improvements in other known routes are of interest. Fischer-Tropsch (F-T) synthesis is an indirect route to catalytic production of liquid fuels from synthesis gas derived from carbonaceous sources. The process is still uneconomical for widespread use due to low space-time-yield (STY), low product selectivity, and catalyst intolerance to sulfur. To address these aspects, a few reports⁴ describe the use of ultrafine particle (UFP) catalysts in slurry-phase F-T synthesis. We recently reported⁵ that a commercially available unsupported UFP Fe_2O_3 material (NANOCAT™) (Mean particle diameter (MPD) = 3 nm; surface area (SA) = 255 m²/g) slurried in a C_{30} hydrocarbon solvent, after reduction at 280°C under CO, catalyzed conversion of balanced synthesis gas ($H_2/CO = 2/1$) at $\geq 220^\circ C$ and ≤ 3 MPa. Described below are additional runs carried out to further scrutinize the Fe UFP system.

EXPERIMENTAL

Unit Description

All runs were carried out in a continuous gas flow unit customized to handle F-T synthesis. The core of the unit was a 1L stirred reactor rated at 40 MPa at 343°C commercially available from Autoclave Engineers (AE). The unit was fitted with a mass flow meter to measure in-flow gas. Before entering the reactor, gas was purified by passing through Scott charcoal and molecular sieve filters. On the reactor head, several gas/liquid ports were provided to allow: 1) inlet gas through a dip tube, 2) catalyst sampling during a run, 3) liquid removal through a 0.5 μ filter to avoid catalyst loss. Unreacted gas and volatile products exited the reactor and passed through a heated line to a 0.5 L hoke bomb, maintained at ambient temperature, where almost all of water and higher hydrocarbons condensed. The remaining gas passed through two 1L and 2L tanks maintained at 5°C and -45°C respectively. The dry gas was vented in a fume hood after passing through a dry test meter.

Analysis

Gases (H_2 , CO, CO_2) were analyzed in the TCD mode under an argon flow on a Gow Mac 580 gas chromatograph fitted with a Poropak R column. Gaseous and liquid hydrocarbons were analyzed in the FID mode under a helium flow on a Perkin Elmer 8500 gas chromatograph fitted with an alumina column, whereas oxygenates in aqueous phase were analyzed in the TCD mode on a Poropak Q column.

Materials

Samples of NANOCAT[™] (α -Fe₂O₃; mean particle diameter (MPD) = 3 nm; surface area (SA) = 255 m²/g; d (bulk) = 0.05 g/mL), from MACH-1, Inc., Ethylflopolyolefin-164 solvent, a dec-1-ene homopolymer (composition: 84.4% trimer, 14.5% tetramer; b.pt. = 518°C; d = 0.818 g/mL; mol. wt. = 437) from Ethyl Corporation, and UCI catalyst (Fe₂O₃ = 69.6, K₂O = 5.1, SiO₂ = 8.3, CuO = 2.6, loss on ignition (LOI) = 14.8, all in wt%; MPD = 32.5 μ m; SA = 232 m²/g from Air Products and Chemicals, Inc. were obtained. Gases were purchased from Scott Specialty Gases.

Catalyst Reduction

A 4.6 wt% NANOCAT[™] in 330 g ethylflopolyolefin-164 solvent was loaded under argon into the 1L AE reactor. The vessel was flushed twice with 0.6 MPa CO before pressurizing to 1.43 MPa. The slurry temperature was slowly raised to 280°C under a 0.2 L/min CO flow. The CO₂ concentration in the exit gas maximized to 4.3 vol% in 5 hours and then decreased to 0.3 vol% at 24 hours. At this time, the catalyst was assumed to be > 95% carbided. A similar CO₂ evolution profile was obtained with the UCI catalyst except that the CO₂ maximum was attained in about 2 hours. A freshly reduced catalyst was used in each run.

F-T Synthesis

After catalyst reduction, the temperature was lowered to a desired value, CO replaced with preblended syngas, and the reactor maintained at a set pressure. Typical reaction conditions were: P = 2.77 MPa; syngas: H₂/CO = 65%/35%; gas hourly space velocity (GHSV) = 5.45-5.75 normal liters (NL).g Fe⁻¹.h⁻¹; stirring speed = 250 rpm.

RESULTS AND DISCUSSION

NANOCAT[™], an unsupported Fe UFP catalyst with MPD of 3 nm, was of interest in this study. Though this was identified as α -Fe₂O₃ by the manufacturer, a recent EXAFS/XANES study⁶ described this material to be iron oxyhydroxide (FeOOH·xH₂O) with surface iron ions having tetrahedral symmetry and water molecules adsorbed on the surface. For data comparison, the UCI catalyst was selected. This supported material contained about 11,000 times larger particles (MPD = 32.5 μ m) of α -Fe₂O₃. For the F-T reaction described here, a low (4.6 wt%) catalyst loading was selected to avoid mass transfer problems at low gas feed rates used. The precursor materials were initially reduced with CO at 280°C to generate the iron carbide phase.⁷ A time profile of CO₂ in the exit gas indicated that reduction beyond 24 hours was unnecessary. Since nature of the pretreatment has a profound effect on catalyst performance,⁷ the same reduction procedure was used in all the runs.

Since the commercial F-T synthesis is carried out at T > 260°C,⁷ performance of the subject catalysts was initially evaluated at 260°C. After the F-T reaction was initiated, CO and H₂ conversions quickly maximized at 91 and 62% respectively. These values dropped to 61 and 52% at 50 hours and then slowly to 44 and 43% at 200 hours. Two subsequent runs at 240° and 220°C showed similar behavior. At 240°C, CO and H₂ conversions were 89, 35, 35% and 62, 38, 32% at 1, 50, 120 hours. At 220°C, the values were 61, 37, 36% and 49, 27, 25% at 5, 50, 200 hours respectively. Since no non-volatile liquid was drained from the reactor during these runs, a decrease in conversion values observed during steady-state (50-200 h) can be attributed to a steady increase in the liquid volume though any contribution from catalyst deactivation cannot be ruled out. The corresponding H₂/CO consumption ratio increased for runs at 260°C

(1.26 (1 h) to 1.81 (200 h)) and 240°C (1.40 (1 h) to 1.87 (120 h)) with time but decreased from 1.45 (5 h) to 1.22 (200 h) at 220°C.

In Table 1, volumetric yield of hydrocarbons produced and CO conversion values are compared as a function of temperature. Though CO conversion increased with Fe UFP with temperature (37.1 and 54.6% at 220 and 260°C respectively), this change was more dramatic with the UCI reference catalyst where the corresponding values changed from 7 to 68.8%. But as shown in Figure 1, any temperature-related increase in CO consumption translated into concomitant increase in hydrocarbons as well as CO₂ concentrations. With Fe UFP, a 17.5% increase in CO consumption shifted the overall product selectivity by a 30.7 wt% decrease in hydrocarbons but a 30.8 wt% increase in CO₂ (Figure 1). With UCI, a 61.8% increase in CO consumption (Table 1) resulted in product selectivity of hydrocarbons and CO₂ changing from 34.3 to 28.8 wt% and 20.3 to 46 wt% respectively. The volumetric yield values showed about 50% increase for Fe UFP but a factor of three for UCI both for C₁-C₄ and C₅+ products (Table 1).

The effect of temperature on hydrocarbon distribution resulting from Fe UFP catalyzed F-T reaction is shown in Table 2. The C₁₁+ fraction decreased with temperature whereas the C₅-C₁₀ and C₂-C₄ fractions showed an increase. CH₄ increased from 10.5 to 17.3 wt% at 220 to 240°C but then decreased to 15.9 wt% at 260°C.

The hydrocarbon product distribution data were used to yield Schulz-Flory plots and α (probability of hydrocarbon chain growth) was calculated from the slope. The α values were 0.56, 0.57, 0.65 (Fe UFP) and 0.53, 0.58, 0.64 (UCI) at 220, 240, 260°C.

In Figure 1, as plotted, the aqueous phase values included oxygenates (5.7, 10.1, 6.0 wt% at 220, 240 260°C). Also, as already reported,⁵ the CO₂ data at 220°C are of interest. During this run, the total CO₂ generated decreased from a high of 23.9% (at 7 h) to 1.44% in 120 hours. Thereafter, no CO₂ was detected in the product stream suggesting no water-gas-shift (WGS) activity. Incidentally, WGS activity could be restored by raising the temperature. A recent⁸ technology review of slurry-phase F-T synthesis with CO-rich synthesis gas suggests the following equation to calculate temperature (T,K) dependence of the equilibrium constant (K_{eq}) for the WGS reaction:

$$K_{eq} = 0.0132 \exp (4578/T) \quad (1)$$

From the presented data of the Fe UFP and UCI systems, some preliminary conclusions are noteworthy. Since the unsupported UFP system permitted a higher iron loading, volumetric efficiency was higher with this system but showed a less dramatic decrease with decreasing temperature. The 220°C data of Fe UFP is of particular interest because the absence of WGS activity was demonstrated with balanced gas. Moreover, the Fe UFP system appeared more stable at 220°C since CO conversion declined less sharply (37 to 36%) compared to that at 260°C (61 to 44%) in 150 hours. Since particle aggregation is a function of temperature,⁷ this phenomenon may explain an overall better performance exhibited by Fe UFP at lower temperatures. EXAFS and Mössbauer data of the final Fe UFP catalyst from the 260°C run showed iron to be in the magnetite phase. Similar and other relevant studies are presently being carried out on these systems and will be the subject of a forthcoming publication.⁹

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Table 1. Volumetric yields and CO conversion as a function of temperature during Fe UFP^a and UCI^a catalyzed F-T synthesis.^b

T, °C	220	240 ^c	260
<u>Fe UFP</u>			
CO conversion, %	37.1	40.8	54.6
Volumetric yield, kg.Lcat ⁻¹ .h ⁻¹			
C ₁ -C ₄	0.008	0.009	0.012
C ₅₊	0.004	0.005	0.006
<u>UCI</u>			
CO conversion, %	7.0	27.0	68.8
Volumetric yield, kg.Lcat ⁻¹ .h ⁻¹			
C ₁ -C ₄	0.003	0.005	0.008
C ₅₊	0.002	0.004	0.006

^aCatalysts were prereduced under 1.43 MPa CO at 280°C for 24 h.

^bTypical F-T conditions were: 4.6 wt% catalyst slurried in 330 g ethylflopolyolefin-164; P = 2.77 MPa; syngas: 65% H₂/35% CO; stirring speed = 250 rpm; space velocity = 5.45-5.75 NL.gFe.⁻¹ h⁻¹. On-line time = 200 h.

^cOn-line time = 120 h.

Table 2. Hydrocarbon product distribution^a as a function of temperature during F-T synthesis^b catalyzed by Fe UFP.

T, °C	220	240	260
C ₁	10.5	17.3	15.9
C ₂ -C ₄	32.0	35.4	38.0
C ₅ -C ₁₀	24.1	28.3	30.1
C ₁₁ +	33.4	19.0	16.0

^aIn wt%.

^bRun conditions same as in the footnotes of Table 1. Data at 120 hours.

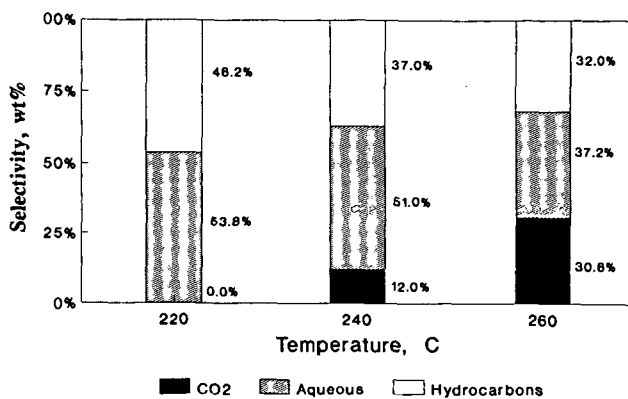


Figure 1. Total product selectivity as a function of temperature. Value shown were at 120 h. The aqueous phase also contained some oxygenates. Reaction conditions were the same as in footnotes of Table 1.